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(71)Applicant : MITSUI CHEM INC
(72)Inventor : SAKURAI SHINJIRO
KUSUMOTO SEIYA

(54) LATEX FOR HEAT SENSITIVE RECORDING MATERIAL, HEAT SENSITIVE RECORDING MATERIAL, AND MANUFACTURE THEREOF

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a heat sensitive recording material, having durability (resistance to water, resistance to oil and the like) which are higher in level than that of a conventional material and provided with a protective layer prominent in stamping property, printing aptitude, color development sensitivity and running stability, and latex for the heat sensitive recording material employed for the same.
SOLUTION: A water soluble resin, obtained by the alkaline resolution of a latex for heat sensitive recording material through a neutralizing agent, is employed for the binder of a protective layer of heat sensitive recording material. The latex for the heat sensitive recording material contains (a) 10-40 wt% of (meth)acrylonitrile, (b) 15-40 wt% of hydroxyalkyl acrylate and (c) 10-40 wt% of (meth)acrylic acid as polymer constituents. In this case, the latex is constituted of a copolymerizate whose total containing amounts of (a), (b), (c) is 60 pts,wt or more and whose glass transition temperature Tg is 10-50° C.

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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] After carrying out the alkali dissolution with a neutralizer, it is the latex for thermal recording ingredients used as a binding material of the protective layer of a thermal recording ingredient. (a) (meta) Acrylonitrile 10 - 40 weight sections, (b) hydroxyalkyl acrylate 15 - 40 weight sections, And the latex for thermal recording ingredients which consists of a copolymer whose Tg the (c) (meta) acrylic acid 10 - 40 weight sections are contained as a polymer component, the sum total of the content of (a), (b), and (c) is more than 60 weight sections, and is -10-50 degree C.
[Claim 2] The latex for thermal recording ingredients according to claim 1 characterized by said neutralizer being ammonia.
[Claim 3] And/or, it sets into the thermal recording ingredient which prepared the protective layer which uses binding material and a filler as a principal component in the rear face of this base material. the heat-sensitive recording layer colored with heat on a base material -- preparing -- further -- a it top -- The binding material of said protective layer is water soluble resin obtained by carrying out the alkali dissolution of the latex for thermal recording ingredients with a neutralizer. This latex for thermal recording ingredients (a) (meta) Acrylonitrile 10 - 40 weight sections, (b) hydroxyalkyl acrylate 15 - 40 weight sections, And the thermal recording ingredient characterized by consisting of a copolymer whose Tg the (c) (meta) acrylic acid 10 - 40 weight sections are contained as a polymer component, the sum total of the content of (a), (b), and (c) is more than 60 weight sections, and is -10-50 degree C.
[Claim 4] The thermal recording ingredient according to claim 3 characterized by said neutralizer being ammonia.
[Claim 5] The thermal recording ingredient according to claim 3 or 4 whose solid content weight content of said filler is the 40 - 200 weight section to said binding-material 100 weight section.
[Claim 6] (A) The process which forms the heat-sensitive recording layer colored with heat on a base material, (B) The process which adds a neutralizer to the latex for thermal recording ingredients, and carries out the alkali dissolution and which is used as water soluble resin, (C) The coating liquid containing this water soluble resin and a filler on said heat-sensitive recording layer It is the manufacture approach of the thermal recording ingredient which applies to the rear face of said base material, and includes the process to dry. And/or, said latex for thermal recording ingredients (a) (meta) Acrylonitrile 10 - 40 weight sections, (b) hydroxyalkyl acrylate 15 - 40 weight sections, And the manufacture approach of the thermal recording ingredient characterized by consisting of a copolymer whose Tg the (c) (meta) acrylic acid 10 - 40 weight sections are contained as a polymer component, the sum total of the content of (a), (b), and (c) is more than 60 weight sections, and is -10-50 degree C.
[Claim 7] The manufacture approach of the thermal recording ingredient according to claim 6 characterized by said neutralizer being ammonia.
[Claim 8] The manufacture approach of a thermal recording ingredient according to claim 6 or 7 that the solid content weight content of said filler is the 40 - 200 weight section to said binding-material 100 weight section.

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the latex for thermal recording ingredients used as a protective layer binding material of the thermal recording ingredient which can record an image by thermal recording, and a thermal recording ingredient.
[0002]
[Description of the Prior Art] Generally a thermal recording ingredient consists of a heat-sensitive recording layer currently formed on the base and this base, by heating by the heat head, the heat stylus, a laser beam, etc., the color coupler in a heat-sensitive recording layer reacts in an instant, and a record image is formed (JP,43-4160,B etc.).
[0003] If such a thermal recording ingredient is used, an image will be obtained only by heating with a heat head, a heat stylus, etc., and a complicated development process will become unnecessary. Moreover, since the record function is prepared in the base materials (paper, a synthetic paper, synthetic-resin film, etc.) of a thermal recording ingredient, a record device serves as compact and comparatively easy structure, and becomes easy [maintenance]. For this reason, it is used for the wide range field as an output record sheet of various printers including facsimile, an industrial use measurement terminal, a medical-application terminal, a handy terminal, a POS system, an issue-of-banknotes system, etc.
[0004] However, the above-mentioned thermal recording ingredient had the following technical problems in everyday handling from being used in various fields.
** When water contacted a thermal recording ingredient, the record layer might fall out.
** When a vinyl chloride film and a sheet were piled up, the vanishment color might arise with the various plasticizers contained in vinyl chloride.
** When fats and oils and a solvent were touched, a vanishment color and coloring might arise.
[0005] That this technical problem should be solved, although various amelioration examination has been made about the binder and coloring ingredient in a heat-sensitive recording layer, that to which all of a water resisting property, plasticizer-proof nature, oilproof oily skin, solvent resistance, etc. are satisfied is not obtained. It is difficult to improve the above-mentioned trouble only by amelioration of the binder in a heat-sensitive recording layer, or a coloring ingredient especially, if it is in the situation that still higher endurance is searched for while application expansion of a thermal recording ingredient is achieved increasingly in recent years.
[0006] Then, the approach of forming a protective layer on a heat-sensitive recording layer is proposed as a measure for this problem (for example, a Provisional-Publication-No. -56126183 [No.] official report, JP,56-13993,A, JP,57-188394,A, etc.).
[0007] However, the protective layer currently indicated with the above-mentioned official report was not what fully fills a demand of the high endurance desired in recent years [of what can raise the endurance of a record layer or a record image to some extent].
[0008] On the other hand, the technique about the following surface protective layer formation agents is indicated by JP,60-059193,A. That is, the technique about the surface protective layer formation agent of a converted paper which blended the epoxy group content cross linking agent with the copolymer salt which consists of a specific rate with carboxyl group content vinyl

monomers, such as acrylamide (meta) and acrylic-acid (meta) low-grade alkyl ester, and which gives oilproof and waterproof shelf life is indicated. Specifically (A) (meta) acrylamide 45-85 (weight) %, (2) (meta) The low-grade alkyl (suitably C1-C4) ester of an acrylic acid, or 10 - 50% more than per sort of hydroxy low-grade alkyl ester And the alkali-metal salt of the copolymer of 5 - 20% more than per sort of the vinyl monomer which has a carboxyl group, The cross linking agent (example; a water-soluble thing is suitable for the diglycidyl ether of a polyethylene glycol etc.) which has the (B) epoxy group is blended with the water solution of ammonium salt or an amine salt. It is supposed that the surface protective layer formation agent which is excellent in a water resisting property, oilproof, etc. will be obtained.

[0009] However, in order to be a water solution before cross linking agent addition and for the surface protective layer formation agent obtained since acrylamide (meta) is an indispensable component and this technique has the high presentation ratio to make a surface protective layer form, the cross linking agent was indispensable.

[0010] Furthermore in recent years, a protection feature and coincidence are increasingly asked for the work as a new functional support layer of a thermal recording ingredient with application expansion at a protective layer. By relation with this, the water resisting property of level still higher than before, oilproof, etc. were searched for from the binding material of a protective layer, and it was not necessarily able to respond to these needs fully with the technique given [above-mentioned] in JP,60-059193,A. This point is explained hereafter.

[0011] As a new function for which a protective layer is asked, the printability to the seal nature (receipt) for example, to an output sheet, a label sheet, etc. is mentioned. Although making inorganic and an organic filler contain in a protective layer is generally performed in order to make such a function discover, it must make it contain these fillers so much to satisfy seal nature and a printability. In this case, that it is easy to produce a paint film defect, in case it becomes or is dealt with in a flexible base material like especially a sheet and a film, the protection feature of a paint film falls to a protective layer -- a crack arises. For this reason, it is difficult to reconcile the function and protection feature as a functional support layer, and the present condition is that the technique of reconciling these is not yet found out.

[0012]

[Problem(s) to be Solved by the Invention] In view of the above-mentioned situation, this invention has the endurance (a water resisting property, oilproof, etc.) of a level still higher than before, and aims at offering seal nature, a printability, the thermal recording ingredient equipped with the protective layer which was further excellent also in coloring sensibility and transit stability, and the latex for thermal recording ingredients used for this.

[0013]

[Means for Solving the Problem] This invention which solves the above-mentioned technical problem is specified according to the matter indicated to the following [1] - [8].

[0014] [1] After carrying out the alkali dissolution with a neutralizer, it is the latex for thermal recording ingredients used as a binding material of the protective layer of a thermal recording ingredient. (a) (meta) Acrylonitrile 10 - 40 weight sections, (b) hydroxyalkyl acrylate 15 - 40 weight sections, And the latex for thermal recording ingredients which consists of a copolymer whose Tg the (c) (meta) acrylic acid 10 - 40 weight sections are contained as a polymer component, the sum total of the content of (a), (b), and (c) is more than 60 weight sections, and is -10-50 degree C.

[0015] [2] The latex for thermal recording ingredients given in [1] characterized by said neutralizer being ammonia.

[0016] [3] And/or, set into the thermal recording ingredient which prepared the protective layer which uses binding material and a filler as a principal component in the rear face of this base material. the heat-sensitive recording layer colored with heat on a base material -- preparing -- further -- a it top -- The binding material of said protective layer is water soluble resin obtained by carrying out the alkali dissolution of the latex for thermal recording ingredients with a neutralizer. This latex for thermal recording ingredients (a) (meta) Acrylonitrile 10 - 40 weight sections, (b) hydroxyalkyl acrylate 15 - 40 weight sections, And the thermal recording ingredient characterized by consisting of a copolymer whose Tg the (c) (meta) acrylic acid 10 - 40 weight

sections are contained as a polymer component, the sum total of the content of (a), (b), and (c) is more than 60 weight sections, and is -10-50 degree C.
[0017] [4] A thermal recording ingredient given in [3] characterized by said neutralizer being ammonia.
[0018] [5] [3] whose solid content weight content of said filler is the 40 - 200 weight section to the binding-material 100 weight section, or a thermal recording ingredient given in [4].
[0019] [6] The process which forms the heat-sensitive recording layer colored with heat on the (A) base material, (B) The process which adds a neutralizer to the latex for thermal recording ingredients, and carries out the alkali dissolution and which is used as water soluble resin, (C) The coating liquid containing this water soluble resin and a filler on said heat-sensitive recording layer It is the manufacture approach of the thermal recording ingredient which applies to the rear face of said base material, and includes the process to dry. And/or, said latex for thermal recording ingredients (a) (meta) Acrylonitrile 10 - 40 weight sections, (b) hydroxyalkyl acrylate 15 - 40 weight sections, And the manufacture approach of the thermal recording ingredient characterized by consisting of a copolymer whose Tg the (c) (meta) acrylic acid 10 - 40 weight sections are contained as a polymer component, the sum total of the content of (a), (b), and (c) is more than 60 weight sections, and is -10-50 degree C.
[0020] [7] The manufacture approach of a thermal recording ingredient given in [6] characterized by said neutralizer being ammonia.
[0021] [8] [6] whose solid content weight content of said filler is the 40 - 200 weight section to the binding-material 100 weight section, or the manufacture approach of a thermal recording ingredient given in [7].
[0022]
[Embodiment of the Invention] The latex for thermal recording ingredients of this invention is used as a binding material of the protective layer of a thermal recording ingredient, after carrying out the alkali dissolution with a neutralizer. In an acid field, it can be dealt with as a latex of hypoviscosity, and since the alkali dissolution can be easily carried out by addition of a neutralizer (alkali) and it can be made aqueous, there is an advantage, such as excelling in handling nature compared with the case where water soluble resin is used as a binder. In addition, it says that a part of latex [at least] dissolves, and "the alkali dissolution" in this invention considers as water soluble resin by addition of alkali, such as ammonia(water). Whenever [alkali meltable / a latex] (the alkali dissolution part to the whole latex comparatively) is the following, and is made and measured. That is, aqueous ammonia can be added to the latex prepared to 10% of solid content, it can be referred to as pH 8.0 [about], the light transmission of the liquid which carried out the alkali dissolution can be measured with a visible spectrophotometer, and it can consider as an index whenever alkali meltable with this value. It is desirable that this light transmission is 30% or more, it is still more desirable that it is 50% or more, and it is most desirable that it is 70% or more (water is made into 100%.). By making the value of light transmission (whenever [alkali meltable]) into the above-mentioned range, adhesive strength to the bulking agent contained in a protective layer is made enough, and many functions as a binding material of a protective layer are demonstrated good. In addition, the approach of measuring viscosity besides the above-mentioned measuring method etc. can estimate whenever [alkali meltable].
[0023] the heat-sensitive recording layer colored with heat on a base material with the thermal recording ingredient in this invention -- preparing -- further -- a it top -- and/or, the record ingredient which prepared the protective layer which uses binding material and a filler as a principal component in the rear face of this base material is said. A heat-sensitive recording layer usually uses electron-donative basic dye and the organic or inorganic electronic receptiveness matter as a principal component, and it comes to allot this binding material, a filler, sensitization material, an unguent, etc. suitably.
[0024] In this invention, the latex for thermal recording ingredients contains (a) (meta) acrylonitrile 10 - 40 weight sections, (b) hydroxyalkyl acrylate 15 - 40 weight sections, and the (c) (meta) acrylic acid 10 - 40 weight sections as a polymer component. Moreover, monomers other than the above can also be included if needed so that it may mention later. Hereafter, each

of these components explain the operation exerted on the property of a thermal recording ingredient etc.

[0025] (Meta) Acrylonitrile shows the effectiveness excellent in improvement in thermal resistance (transit stability), plasticizer-proof nature, oilproof, and organic solvent-proof nature. (Meta) The amount of the acrylonitrile used is 10 - 40 % of the weight among the solid content 100 weight section of the latex for thermal recording ingredients, and is 15 - 35 % of the weight preferably. (Meta) The thermal resistance which needs the amount of the acrylonitrile used at less than 10 % of the weight is not obtained, trouble is caused to transit stability and still more sufficient plasticizer-proof nature may not be obtained. If it exceeds 40 % of the weight, even if it neutralizes, it is not made aqueous, but there is a case where a polymerization will not advance to stability, either.

[0026] Hydroxyalkyl acrylate has the role which gives moderate flexibility, holding plasticizer-proof nature. As a rate of occupying in the latex for thermal recording ingredients, it is 15 - 40 % of the weight, and is 20 - 30 % of the weight preferably. At less than 15 % of the weight, required flexibility is missing, and when it exceeds 40 % of the weight, while a hydrophilic property increases and it becomes impossible to maintain the gestalt as an emulsion, a water resisting property also gets worse.

[0027] (Meta) By introducing a carboxy group into the resin frame of the latex for thermal recording ingredients, an acrylic acid gives alkali fusibility and has the role which uses a latex as water soluble resin by addition of a neutralizer. By changing a latex to water soluble resin, the affinity to a filler improves remarkably and the protective layer excellent also in the bottom of a lot of filler content can be formed. Moreover, it acts useful as a functional group of the low-temperature cross linking agent added as occasion demands. (Meta) The amount of the acrylic acid used is 10 - 40 % of the weight among the latex for thermal recording ingredients, and is 15 - 30 % of the weight preferably. Alkali fusibility sufficient at less than 10 % of the weight is not acquired, but the stability of the water soluble resin obtained is also inferior. When it exceeds 40 % of the weight, coloring (fogging) may arise in a sensible-heat layer.

[0028] Moreover, the above-mentioned monomer and the monomer of others which can be copolymerized can also be included if needed. A suitable monomer is chosen, by including in a suitable amount and polymer component, the manufacture stability of the latex for thermal recording ingredients can be raised, and a water resisting property can be raised.

[0029] The amount of this monomer used is preferably made into less than 25 % of the weight less than 40% of the weight among the latex for thermal recording ingredients. If 40 % of the weight is the above, it will become difficult [that plasticizer-proof nature gets worse and a water resisting property gets worse depending on the case etc.] to balance a water resisting property and plasticizer-proof nature. As an example of this monomer, a methyl acrylate (meta), an ethyl acrylate (meta), Butyl acrylate, acrylic-acid (meta) lauryl, methacrylic acid 2-hydroxyethyl, (Meta) Methacrylic acid 2-hydroxypropyl, methacrylic acid 2-hydroxy butyl, Acrylic-acid 2-aminoethyl, acrylic-acid (meta) 2-(N-methylamino) ethyl, (Meta) Acrylic ester (meta), such as acrylic-acid 2-(N and N-dimethylamino) ethyl and metaglycidyl acrylate (meta), (Meta) Unsaturated carboxylic acid, such as a maleic anhydride, boletic acid, an itaconic acid, and a crotonic acid N-permutation unsaturated-carboxylic-acid amides, such as aromatic series vinyl monomers, such as styrene, alpha methyl styrene, and a divinylbenzene, acrylamide (meta), and N-methylol (meta) acrylamide, etc. are mentioned. Comparatively oleophilic things, such as long (meta) acrylic ester of styrene and/or alkyl chain length, are used preferably especially.

[0030] The glass transition point of the latex for thermal recording ingredients in this invention is -10-50 degrees C, and is 0-30 degrees C preferably. It becomes easy to produce the so-called sticking phenomenon in which a protective layer sticks to a heat head that a glass transition point is less than -10 degrees C since thermal resistance is not enough. On the other hand, since a protective layer will become weak if it exceeds 50 degrees C, when a soft sheet is especially used as a base material, in case it is dealt with, a crack may arise in a protective layer and the target function may be spoiled.

[0031] Although especially the mean particle diameter of the latex for thermal recording ingredients of this invention does not have a limit, let it preferably be the range of 100-300nm

still more preferably 50-500nm. In less than 50nm, the viscosity of a system may become remarkably high, resin concentration at the time of manufacture must be made low in this case, and it becomes disadvantageous on economy. Moreover, when alkali is added, since surface area is large, solubilization may progress partially, it may become mama powder, and uniform solubilization may become difficult. On the other hand, if it exceeds 500nm, since surface area is large, solubilization time amount may become long and may pose an activity top problem.

[0032] That what is necessary is just to follow a well-known emulsion-polymerization technique, if needed, in order to give polymerization stability, an emulsifier can be used for the method of obtaining the latex for thermal recording ingredients of this invention. For example, nonionic surface active agents, such as anionic surface active agents, such as a sulfate of higher alcohol, alkylbenzene sulfonates, an aliphatic series sulfonate, and an alkyl diphenyl ether sulfonate, an alkyl ester mold of a polyethylene glycol, an alkylphenyl ether mold, and an alkyl ether mold, can also be used in independent or two or more sorts of combination. About the amount of these emulsifiers used, although there is nothing, when the water resisting property of resin is taken into consideration, as for especially a limit, considering as the need minimal dose is desirable.

[0033] Furthermore, as a polymerization initiator used in case the polymerization of the latex for thermal recording ingredients is carried out, what is used for the usual emulsion polymerization is mentioned. As these, oil solubility initiators, such as water-soluble initiators, such as persulfate and a hydrogen peroxide, azobisisobutyronitril, and a benzoyl peroxide, or a redox system initiator is used. Although what is necessary is for there to be especially no limit about the amount of a polymerization initiator, and just to follow a well-known technique, it is used in the range of 0.1 - 10 weight section to the monomer 100 weight section, and is 0.1 - 5 weight section preferably.

[0034] Moreover, as a molecular-weight modifier (chain transfer agent), mercaptans, such as t-dodecyl mercaptan, n-dodecyl mercaptan, and an octyl mercaptan, an alpha-methyl-styrene dimer, a low-molecular halogenated compound, etc. are used if needed. Although molecular weight can be prepared with these amount used, since viscosity will become remarkably high and trouble will be caused to workability when the alkali dissolution of the latex for thermal recording ingredients is carried out with a neutralizer if molecular weight is too high, when it considers as water-solution viscosity 10%, it is desirable to consider as the molecular weight which becomes the range of a 100-3000mm pascal.

[0035] By using the resin which made aqueous the latex for thermal recording ingredients obtained by the above with the neutralizer as a binding material of a protective layer, it has the outstanding endurance and seal nature, a printability, and the thermal recording ingredient that was further excellent also in coloring sensibility and transit stability can be obtained.

[0036] As a neutralizer added in order to make aqueous the latex for thermal recording ingredients of this invention, ammonia (aqueous ammonia) is used suitably. As other examples, although a sodium hydroxide, a potassium hydroxide, and various amines are mentioned, it is desirable to avoid use. It is because the object for the hyposensitization at the time of heat coloring will become large if a water resisting property is reduced, a heat head may be damaged, when a sodium hydroxide and a potassium hydroxide are used, and various amines are used. When aqueous ammonia is used, since such a problem does not occur and it is comparatively easy to break away at low temperature, a good water resisting property is obtained after the protection stratification.

[0037] As a filler in this invention, organic particles, such as inorganic fillers, such as a kaolin, a baking kaolin, talc, a calcium carbonate, a magnesium carbonate, titanium oxide, a zinc oxide, silicon oxide, and an aluminum hydroxide, urea-formalin resin, and polystyrene impalpable powder, are mentioned, and it is used in a kind or two sorts or more of combination, for example. However, since printing concentration may become low if the obliterating power of a bulking agent is too large, it is necessary to choose a class and an addition suitably so that trouble may not be given to printing concentration.

[0038] The amount of the filler used is the 60 - 150 weight section preferably [it is desirable and] to the 40 - 200 weight section and a pan to the latex 100 weight section for thermal recording ingredients. Transit stability and seal nature may not fully be obtained under in 40 weight sections. On the other hand, if the 200 weight sections are exceeded, a bulking agent may

not fully be combined and plasticizer-proof nature, solvent resistance, and a printability may not fully be acquired.

[0039] Lubricant, such as a higher-fatty-acid metal salt for raising more a deck-watertight-luminaire-ized agent (cross linking agent) and sticking-proof nature as a component used if needed besides a filler, a higher-fatty-acid amide, and a polyolefine particle of high crystallinity, an ultraviolet ray absorbent, an antioxidant, a defoaming agent, a wetting agent, PH modifier, a viscosity modifier, other assistants, and additives are mentioned.

[0040] Since heat head fitness (sticking nature, transit stability) can be raised more, it is suitably used, at the same time a deck-watertight-luminaire-ized agent (cross linking agent) strong-izes a protective layer more and makes the endurance of a sensible-heat layer and a record image improve much more especially. As an example of such a cross linking agent, glyoxal, a dimethylolurea, the glycidyl ether of polyhydric alcohol, a ketene dimer, dialdehyde starch, the epichlorohydrin denaturation object of a polyamide amine, carbonic acid zirconium ammonium, an aluminum sulfate, a calcium chloride, boric acid, etc. are mentioned.

[0041] Although the resin which made the latex for thermal recording ingredients aqueous is used for the binding material of the thermal recording ingredient of this invention, it may be used together with other well-known binding material as occasion demands. As such a binding material, generally, although it can be used [for the purpose of well-known natural resin (for example sodium alginate, starch, casein, and celluloses) or synthetic resin], the denaturation object of polyvinyl alcohol is desirable, for example, carboxyl group denaturation, the aceto acetyl group denaturation, epoxy group denaturation, silanol group denaturation, amino-group denaturation, olefin denaturation, amide denaturation, NIRORIRU denaturation, etc. are mentioned as an example of those denaturation objects especially.

[0042] The part which applies the binding material which used the latex for thermal recording ingredients of this invention is not restricted to the rear face of a base material on a heat-sensitive recording layer, but can be suitably applied to the part which may raise the function of a protective layer.

[0043] Moreover, especially the coloring system of the heat-sensitive recording layer section by which this invention is applied is not limited, either. Incidentally, as these coloring system, there are a thing using the acid represented by a leuco color and the phenol nature matter, a thing using an imino compound and an isocyanate compound, a thing using a diazo compound and a coupler, etc.

[0044] As for the protective layer of this invention, it is desirable to be applied by an air knife coater, a gravure coating machine, a roll coater, the rod coating machine, etc. two times one to 10 g/m by the weight after desiccation between the well-known heat-sensitive recording layer top usually established in paper, a synthetic paper, and film superiors as a base material and/or the rear face of a base material, a base material, and a heat-sensitive recording layer.

[0045] Hereafter, this invention is not limited by the examples of many [these] although the example of manufacture and the example of comparison manufacture, an example, and the example of a comparison explain this invention concretely. In addition, number of copies in many following examples and % express weight section and weight %, especially when [all] there is no assignment.

[0046]

[Example] (Manufacture of the latex for thermal recording ingredients)

After it taught the water 146 section, the sodium dodecylbenzenesulfonate 0.1 section, and the potassium persulfate 1.0 section to the separable flask example of manufacture A1 agitator, and with a ring current cooler and nitrogen gas permuted with it, the temperature up was carried out to 70 degrees C. Subsequently, after adding the emulsification object of the following presentation continuously over 4 hours, temperature was raised to 80 degrees C, it held for 3 hours, and the polymerization was completed. The appearance of the obtained aquosity copolymerization resin was the emulsion of opalescence, and, as for a 10mm pascal and PH, the nonvolatile matter of viscosity was 4.5 35%.

[0047] Monomer emulsification constituent acrylonitrile 30 section hydroxyethyl acrylate 20 section hydroxypropyl acrylate 5 section methacrylic acid 20 section butyl acrylate 20 section

styrene 5 section n-dodecyl mercaptan 1 **** 40 section sodium dodecylbenzenesulfonate Make it be the same as that of the example A1 of manufacture except having changed the examples A2-A7 of 0.1 section manufacture and the example B1 of comparison manufacture - B7 monomer presentation. The latexes A2-A7 for thermal recording ingredients and the examples B1-B7 of comparison manufacture were manufactured. A presentation and a result are collectively shown in Table 1.

[0048] The valuation basis of front Naka, a glass transition point (Tg), polymerization stability, and alkali solubility is as follows.

[0049] (Glass transition point) Glass transition temperature (Tg) was measured by the differential scanning calorimetry (DSC).

[0050] (Polymerization stability)

O : it is the stable emulsion particle which shows the appearance of opalescence, and there are not generating of the floc at the time of manufacture, an affix to an impeller, and generating of residue.

**: Although the stable emulsion particle which shows the appearance of opalescence is obtained, some aggregate has adhered to the impeller at the time of manufacture. Or at the time of manufacture, a lot of water-soluble polymers generate, and the viscosity in a system becomes remarkably high.

x: Generating of floc is abundant and manufacture is difficult.

[0051] (Alkali solubility) It adds to the latex prepared so that solid content might become 10%, agitating aqueous ammonia for the purpose of pH8.0 28%, and the alkali dissolution is performed to it. The dissolution degree was measured with light transmission with a wavelength of 550nm in the glass cel of 10mm of optical path lengths using spectrophotometer for ultraviolet and visible region (the Shimadzu make, UV-600). When light transmission of deionized water was made into 100%, it judged on the following criteria.

O : light transmission 70%[more than] **: Light transmission Less-than [70% 30% or more] x: Light transmission It explains per [which used the examples A1-A7 of manufacture, and the examples B1-B7 of comparison manufacture for the protective layer, and used them as the thermal recording ingredient next less than 30%] example. Also in which example, a presentation is the weight section. In addition, B-2 which the problem produced at polymerization stability was not applied to the following examples among the example of comparison manufacture.

[0052] The water 250 section was added to the latex 100 section for thermal recording ingredients obtained in the example A1 of example 1 manufacture, 28% of aqueous ammonia was gradually added for the purpose of PH8 after dilution, and the latex for thermal recording ingredients was dissolved underwater. Furthermore, mixed distribution of the water the impalpable powder silica (product made from Mizusawa chemistry: Ms. KASHIRU P-527) 35 section and for viscosity preparation was carried out in the sand mill after optimum dose ****** there for 3 hours, and coating liquid was obtained. Next, the zinc stearate dispersion-liquid 8 section was added to this coating liquid 30%, after mixing again so that it might become homogeneity, spreading desiccation was carried out in the bar coating machine so that it might become 3 g/m2 in a commercial facsimile form with dry weight (it is recuperated for seven days under 20 degrees C / 65%RH ambient atmosphere after a 30-second forced drying at 60 degrees C), and the thermal recording ingredient was obtained.

[0053] The thermal recording ingredient of the example 2 of this invention was obtained like the example 1 having used the latex for thermal recording ingredients obtained in example A5 of example 2 manufacture, and except having used the precipitated-calcium-carbonate (Maruo Calcium) 14 section instead of the impalpable powder silica 35 section. In addition, in this example, the alkali fusibility of the latex at the time of adding aqueous ammonia was a little inadequate.

[0054] The thermal recording ingredient was obtained like the example 1 having used the latex for thermal recording ingredients obtained by example A4 of example 3 manufacture, and except having used the precipitated-calcium-carbonate 52.5 section instead of the impalpable powder silica 35 section.

[0055] The thermal recording ingredient was obtained like the example 1 instead of having used

the latex for thermal recording ingredients obtained in the example A2 of example 4 manufacture, and the impalpable powder silica 35 section except having added the aquosity epoxy system resin (Mitsui Chemicals [, Inc.] make: you lamin P-5600) 12 section to the dispersion liquid made into the precipitated-calcium-carbonate 28 section as a cross linking agent. In addition, in this example, the alkali fusibility of the latex at the time of adding aqueous ammonia was a little inadequate.

[0056] The thermal recording ingredient was obtained like the example 1 except having added the carbonic acid zirconium ammonium 13% water-solution (product made from first Rare element: JIRUKOZORU AC-7) 14 section to having used the latex for thermal recording ingredients obtained by example A3 of example 5 manufacture, and the dispersion liquid made into the aluminum-hydroxide (Showa Denko: H-42) 24.5 section instead of the impalpable powder silica 35 section as a cross linking agent.

[0057] The thermal recording ingredient was obtained like the example 1 having used the latex for thermal recording ingredients obtained in the example A6 of example 6 manufacture, and except having considered as the barium-sulfate (Sakai Chemical Industry: BARIFAIN BF-1) 42 section instead of the impalpable powder silica 35 section.

[0058] The thermal recording ingredient was obtained like the example 1 except having added the glycidyl ether (Nagase: DENAKORU 512) 3.5 section of polyhydric alcohol as a cross linking agent to having used the latex for thermal recording ingredients obtained in the example A7 of example 7 manufacture, and the dispersion liquid made into the kaolin (en gel hardware: UW-90) 17.5 section instead of the impalpable powder silica 35 section.

[0059] The thermal recording ingredient of the example 1 of a comparison was obtained like the example 1 except having used the latex for thermal recording ingredients obtained in the example B1 of example of comparison 1 comparison manufacture. In addition, in this example of a comparison, the alkali fusibility of the latex at the time of adding aqueous ammonia was a little inadequate.

[0060] The thermal recording ingredient was obtained like the example 4 except having used the latex for thermal recording ingredients obtained in the example B3 of example of comparison 2 comparison manufacture. In addition, in this example of a comparison, when it adds, the alkali fusibility of a latex is inadequate, and aqueous ammonia was not water-solubility-ized.

[0061] The thermal recording ingredient was obtained like the example 3 except having used the latex for thermal recording ingredients obtained by example B4 of example of comparison 3 comparison manufacture. In addition, in this example of a comparison, the alkali fusibility of the latex at the time of adding aqueous ammonia was a little inadequate.

[0062] The thermal recording ingredient was obtained like the example 2 except having used the latex for thermal recording ingredients obtained in example B5 of example of comparison 4 comparison manufacture.

[0063] The thermal recording ingredient was obtained like the example 4 except having used the latex for thermal recording ingredients obtained in example B6 of example of comparison 5 comparison manufacture. In addition, in this example of a comparison, before adding aqueous ammonia to a latex, it was already in the half-water meltable condition.

[0064] The thermal recording ingredient was obtained like the example 4 except having used the latex for thermal recording ingredients obtained in the example B7 of example of comparison 6 comparison manufacture.

[0065] As mentioned above, the following approaches estimated the thermal recording ingredient obtained in examples 1-7 and the examples 1-6 of a comparison. An evaluation result is shown in Table 1 and Table 3.

(1) The thermal recording side which applied the section non-colored [waterproof] and a 140-degree C heat block for 1 second, and colored them was rubbed 20 times with the gauze in which water was included using the **** type friction strong testing machine (however, weighting [no] use), and viewing estimated the condition of a thermal recording side.

O : don't change.

O : the marks rubbed a little remain.

**: It is missing a little.

x: It is missing.
(2) One drop of tempura oil was dropped to the thermal recording side colored like the oilproof above, further, with gauze, as it wiped off lightly, it extended, and viewing estimated the fading degree after 6-hour neglect at the room temperature. O : don't fade.
**: It is fading a little.
x: It is fading considerably.
(3) The transparence type polyvinyl chloride adhesive tape for electric insulation (NITTO DENKO make) was stuck on the thermal recording side colored like the plasticizer-proof nature above, after leaving it at 40 degrees C for 24 hours, it removed, and the concentration of the non-tape attachment section and the tape attachment section was measured with the Macbeth concentration meter, and concentration retention (%) was computed by the degree type (so good that it is expensive).
The concentration retention (%) =(Macbeth concentration of the tape attachment section) / (Macbeth concentration of the non-tape application attachment section) x100(4) solvent-resistance non-coloring side was traced with the gauze into which ethanol was infiltrated, and viewing estimated the coloring degree.
O : don't color.
**: Color a little.
x: Color.
(5) Transit stability (sticking-proof nature)
The sensible-heat printer (Ohkura Electric TH-PND) was used, it printed according to the following conditions, and the dirt condition of extent of the sound at that time (decrepitation) and a head was evaluated synthetically.
applied voltage :24V pulse width : 1.74ms impression energy: -- 0.34mj/dot O: -- there is not a sound, but there is also no head dirt, and paper feed is smooth.
**: Although there is a sound a little, there is also no head dirt and paper feed is also convenient.
x: Putty putty and a sound are loud. Head dirt is seen and they are those with trouble to paper feed.
(6) It printed on conditions like the coloring sensibility above, and the concentration of a printing side was measured with the Macbeth concentration meter.
(7) Make the thermal recording side side of chip box-proof crack **** coloring into a table, and set this to two in the inside of a finger lightly at a chip box. Next, after changing to the whole surface, the fold part by the side of a recording surface was traced with the oily light color marker (the product made from a zebra: yes maqui (yellow)), and the chip box crack degree of a protective layer was observed. Since the organic solvent in a marker sank in and colored all over the heat-sensitive recording layer when the chip box crack occurred, viewing estimated the extent.
O : with no generating of a chip box crack.
**: They are those with a chip box crack a little.
x: A chip box crack occurs along with a fold.
(8) The seal nature thermal recording side side was sealed by having used Shachihata X stamper ink (Shachihata, Inc. make), and viewing estimated the blot degree of gauze grinding and the seal section for a it top immediately after.
O : change is not looked at by the seal section.
**: A blot occurs a little in the seal section.
x: The seal section can bleed and cannot read.
(9) Using the printability RI printability testing machine (Meiji Drop Forge), it printed in ink (Toyo Ink make: SMX tuck 25), and viewing estimated the peeling (picking) degree of a protective layer.
O With no generating of :picking.
**: -- some picking generating x: -- a picking -- generating.
[0066]
[Table 1]

（表－１） 製造例 Ａ－１～Ａ－７、および比較製造例Ｂ－１～Ｂ－７

成分	組 成	製造例							比較製造例						
		A-1	A-2	A-3	A-4	A-5	A-6	A-7	B-1	B-2	B-3	B-4	B-5	B-6	B-7
a	アクリロニトリル	30		35	15	40	10	35		10	35	10	35		
	メタアクリロニトリル		10		10				30						
b	ヒドロキシエチルアクリレート	20		30		30	25	10		25	35		30	20	20
	ヒドロキシプロピルアクリレート	5	5						5	25	10	20		5	5
	ヒドロキシブチルアクリレート		15	10	30			25	10			20			
c	アクリル酸				10	20	20					10			
	メタアクリル酸	20	30	10	10		20	30	10	20	5		25	20	20
d	ブチルアクリレート	20	40	10	25	5	20		30	20	10	30		5	20
	スチレン	5		5		5	5		15		5	10	10	5	5
	アクリルアミド													45	
	メチルメタアクリレート														30
a ＋ b ＋ c		75	60	85	75	90	75	100	55	80	85	60	90	45	45
Tg（℃）		31	-2	18	-10	50	29	26	24	6	25	-21	65	38	30
エマルジョン重合安定性		○	○	○	○	△	○	△	○	×	○	○	○	△	○
アルカリ可溶性		○	○~△	○	○	△	○	○	△	供試せず	×	△	○	既半溶解	○

[0067]
[Table 2]
（表－２）製造例Ａ－１～Ａ－７、および比較製造例Ｂ－１～Ｂ－７

	製造例又は比較製造例	充填材種	結合剤／充填材（乾燥重量比）	中和剤	架橋剤
実施例－1	A1	微粉末シリカ	100/100	アンモニア	
実施例－2	A5	軽質炭酸カルシウム	100/40	アンモニア	
実施例－3	A4	軽質炭酸カルシウム	100/150	アンモニア	
実施例－4	A2	軽質炭酸カルシウム	100/80	アンモニア	ユーラミンP5600
実施例－5	A3	水酸化アルミニウム	100/70	アンモニア	ジルコゾールAC-7
実施例－6	A6	硫酸バリウム	100/120	アンモニア	
実施例－7	A7	カオリン	100/50	アンモニア	デナコール512
比較例－1	B1	微粉末シリカ	100/100	アンモニア	
比較例－2	B3	軽質炭酸カルシウム	100/80	アンモニア	P5600
比較例－3	B4	軽質炭酸カルシウム	100/150	アンモニア	
比較例－4	B5	軽質カルシウム	100/40	アンモニア	
比較例－5	B6	軽質炭酸カルシウム	100/80	アンモニア	P5600
比較例－6	B7	軽質炭酸カルシウム	100/80	アンモニア	P5600

備考：比較製造例B2は重合安定性が著しく悪く、供試しなかった。

[0068]
[Table 3]
（表－3）製造例A－1～A－7、および比較製造例B－1～B－7

	耐水性	耐油性	濃度保持率(%)	耐溶剤性	走行安定性	発色感度	耐折り割れ性	捺印性	印刷適性	その他
実施例－1	○	○	100	○	○	1.37	○	○	○	
実施例－2	○	△	92	△	○	1.40	○	○	△	
実施例－3	○	○	95	○	○	1.30	△	○	○	
実施例－4	◎	○	75	○	△	1.30	○	○	○	
実施例－5	◎	○	95	△	○	1.34	△	○	○	
実施例－6	○	○	93	○	○	1.40	○	○	○	
実施例－7	○	○	100	○	○	1.41	○	△	○	若干かぶり
比較例－1	◎	△	10	△	○	1.29	○	○	○	
比較例－2	◎	×	0	×	○	1.24	○	○	×	
比較例－3	○	○	0	○	×	1.40	○	△	○	
比較例－4	○	○	100	○	○	1.42	×	△	×	
比較例－5	×	○	78	△	△	1.32	△	○	△	
比較例－6	△	○	35	○	○	1.06	△	○	○	

[0069]
[Effect of the Invention] As explained above, since the latex for thermal recording ingredients of this invention is carrying out specific number-of-copies use of the specific monomer, while it is excellent in alkali fusibility and polymerization stability, when it uses as a binding material of the protective layer of a thermal recording ingredient, it can raise remarkably the endurance under many environments where a thermal recording object is used, and seal nature and a printability.
[0070] Moreover, since the thermal recording ingredient of this invention uses the above-mentioned latex for thermal recording ingredients for the binding material of a protective layer, it is excellent in the endurance under many environments, seal nature, and a printability, and can do the applied thing to an extensive field.
[0071] Moreover, the manufacture approach of the thermal recording ingredient of this invention makes what carried out the alkali dissolution of the above-mentioned latex for thermal recording ingredients, and was used as water soluble resin contain in coating liquid, and since the process of applying this to a predetermined part is taken, it can be manufactured simple, without passing through a complicated process the thermal recording ingredient which has the above advantages.

[Translation done.]